JOURNAL OF MATERIALS SCIENCE 37 (2002) 5237–5240

Third-order elastic constants and pressure derivatives of the second-order elastic constants of hexagonal boron nitride

V. M. MATHEW, C. S. MENON, K. P. JAYACHANDRAN
School of Pure and Applied Physics, Mahatma Gandhi University, Kottayam, Kerala, India 686 560
E-mail: spapf@sancharnet.in

The second and third order elastic constants and pressure derivatives of second order elastic constants of hexagonal boron nitride have been obtained using the deformation theory. The strain energy derived using the deformation theory is compared with the strain dependent lattice energy obtained from elastic continuum model approximation to get the expressions for second and third order elastic constants. Higher order elastic constants are a measure of anharmonicity of crystal lattice. The six second-order elastic constants and the ten non-vanishing third order elastic constants and six pressure derivatives of hexagonal boron nitride are obtained in the present work and are compared with available experimental values. The second order elastic constant C_{11} which corresponds to the elastic stiffness along the basal plane of the crystal is greater than C_{33}. Since C_{33} being the stiffness tensor component along the *c*-axis of the crystal, this result is expected from a layer-like material like boron nitride (BN). The third order elastic constants of hexagonal BN are generally one order of magnitude greater than the second-order of elastic constants as expected of a crystalline solid. The pressure derivative dC_{33}/dp obtained in the present study is greater than dC_{11}/dp which indicates that the compressibility along *c*-axis is higher than that along *ab*-plane of hexagonal BN.

1. Introduction

Knowledge of higher order elastic constants like second and third order elastic constants is essential for the study of the anharmonic properties of solids. The hexagonal crystals have six second order elastic constants and ten third order elastic constants. Elastic constants also provide insight into the nature of binding forces between the atoms since they are represented by the derivatives of the internal energy.

As with a number of technologically useful materials a growth of the diversity of the application of boron nitride has led to a desire to understand its fundamental properties fully. This has resulted in the investigation of a variety of physical properties [1–11], attempts at explaining some of which have been made subsequently with reference to the corresponding behaviour of pyrolytic graphite, the lamellar structure of which resembles that of the hexagonal form of born nitride. Although several attempts at evaluating the second-order elastic constants [12, 13] theoretically were made, there is hardly any measurement on the complete set of the second-order as well as third order elastic constants of hexagonal boron nitride.

In this paper, the expressions for the second order and third order elastic constants of hexagonal crystals are derived using the sublattice displacements up to first order in strains. The expression for the effective second-order elastic constants based on finite strain elasticity theory in terms of the second and third order elastic constants have been worked out for hexagonal crystals. These expressions are used to obtain the first order pressure derivatives of the second order elastic constants of hexagonal BN.

2. Second and third order elastic constants

Considering interactions up to second neighbours, the potential energy of hexagonal BN per unit cell is

$$\phi = \phi_0 + \sum_{I=1}^{6} \phi R(I) + \sum_{j=1} \phi R(J) \qquad (1)$$

Here, I atoms are the six neighbours of the same type in the basal plane and J atoms are the six non-equivalent atoms which are out of the basal plane. Here ϕ_0 is the static potential energy of the crystal.

The components of interatomic vector **R** after deformation are given by

$$R_i'(I) = R_i(I) + \sum_j \in_{ij} R_j(I)$$

$$R_i'(J) = R_i(J) + \sum_j \in_{ij} R_j(J) + W_i \qquad (2)$$

Here $\in_{ij}$ are the deformation parameters and are related to the macroscopic Lagrangian strains by

$$\eta_{ij} = \frac{1}{2}\left(\in_{ij} + \in_{ij} + \sum_k \in_{ki} \in_{kj} \right) \tag{3}$$

W_i are the components of the internal displacements of the lattice of particles of the type J relative to the lattice of particles of the type I and are replaced by the relative internal displacements $\bar{W}_i$ by the relation.

$$\bar{W}_i = W_i + \sum_j \in_{ji} W_j \tag{4}$$

The potential energy is expanded in powers of the changes in squares of the vector distances $R(I)$ and $R(J)$ as

$$\phi = \phi_0 + k_2\left[\sum_I [\Delta R^2(I)]^2 + \sum_J [\Delta R^2(J)]^2 \right] + k_3\left[\sum_I [\Delta R^2(I)]^3 + \sum_J [\Delta R^2(J)]^3 \right] + \cdots \tag{5}$$

Here k_2 is the second order harmonic parameter and k_3 is the third order anharmonic potential parameter respectively.

The strain energy derived from continuum model approximation (14) is

$$U = \frac{1}{2!} C_{ijkl}\, \eta_{ij}\, \eta_{kl} + \frac{1}{3!} C_{ijklmn}\, \eta_{ij}\, \eta_{kl}\, \eta_{mn} + \cdots \tag{6}$$

where C_{ijkl} and C_{ijklmn} are the second order and third order elastic constants in the tensor notation.

Comparing this with the lattice energy from Equation 5 we get the expressions for second and third-order elastic constants in Voigt's notation of hexagonal boron nitride, as

$$C_{11} = \frac{116}{3}\frac{D^4 k_2}{V_a} \tag{7a}$$

$$C_{12} = \frac{41}{8}\frac{D^4 k_2}{V_a} \tag{7b}$$

$$C_{13} = \frac{5}{3}p^2\frac{D^4 k_2}{V_a} \tag{7c}$$

$$C_{33} = 3p^4\frac{D^4 k_2}{V_a} \tag{7d}$$

$$C_{44} = 2p^2\frac{D^4 k_2}{V_a} \tag{7e}$$

$$C_{66} = \frac{63}{8}\frac{D^4 k_2}{V_a} \tag{7f}$$

$$C_{111} = \frac{1099}{10}\frac{D^6 k_3}{V_a} + \frac{23}{3}\frac{D^4 k_2}{V_a} \tag{8a}$$

$$C_{112} = \frac{83}{5}\frac{D^6 k_3}{V_a} - \frac{7}{5}\frac{D^4 k_2}{V_a} \tag{8b}$$

$$C_{113} = \frac{5}{3}p^2\frac{D^6 k_3}{V_a} + p^2\frac{D^4 k_2}{V_a} \tag{8c}$$

$$C_{123} = \frac{7}{5}p^2\frac{D^6 k_3}{V_a} - p^2\frac{D^4 k_2}{V_a} \tag{8d}$$

$$C_{133} = \frac{16}{5}p^4\frac{D^6 k_3}{V_a} \tag{8e}$$

$$C_{144} = 2p^2\frac{D^6 k_3}{V_a} \tag{8f}$$

$$C_{155} = \frac{4}{3}p^2\frac{D^6 k_3}{V_a} \tag{8g}$$

$$C_{222} = \frac{175}{2}\frac{D^6 k_3}{V_a} + \frac{39}{5}\frac{D^4 k_2}{V_a} \tag{8h}$$

$$C_{333} = \frac{9}{2}p^6\frac{D^6 k_3}{V_a} \tag{8i}$$

$$C_{344} = 3p^4\frac{D^6 k_3}{V_a} \tag{8j}$$

where V_a is the volume of the unit cell, D is the nearest neighbour distance and p is the axial ratio c/a. The potential parameter k_2 has been obtained by substituting the value of $C_{33} = 32.4$ GPa measured by Green *et al.* [2] in Equation 7d and k_2 thus obtained is given in Table II.

The values of second order elastic constants of hexagonal BN are obtained by substituting this value of k_2 in Equations 7 and are given in Table I along with the other reported values.

The third-order anharmonic parameter k_3 in Equation 8 is evaluated by substituting the value of $C_{333} = -589.6$ GPa measured by Green *et al.* [2] in Equation 8i. The value of k_3 thus obtained is given in Table II. Substituting the values of k_2 and k_3 from Table II in Equations 8 we get the third-order elastic constants of hexagonal BN. The values of third-order elastic constants thus obtained for hexagonal BN are given in Table III.

TABLE I Second order elastic constants of hexagonal BN (in GPa)

C_{ij}	Present work	Experimental value [2]	Calculated value [15]
C_{11}	55.5	–	–
C_{12}	7.4	–	–
C_{13}	6.6	–	–
C_{33}	32.4	32.4	–
C_{44}	7.9	–	6.2
C_{66}	11.3	–	–

TABLE II Values of potential parameters k_2 and k_3 for hexagonal BN

$\frac{k_2 D^4}{V_a}$ (GPa)	$\frac{k_3 D^6}{V_a}$ (GPa)
1.436	−6.353

TABLE III Third order elastic constants of hexagonal BN (in GPa)

C_{ijk}	Present work	Experimental value [2]
C_{111}	−687.2	–
C_{112}	−107.5	–
C_{113}	−25.1	–
C_{123}	−28.3	–
C_{133}	−152.9	–
C_{144}	−34.8	–
C_{155}	−23.2	–
C_{222}	−544.7	–
C_{333}	−589.6	−589.6
C_{344}	−143.3	–

3. Pressure derivatives of the second-order elastic constants of hexagonal BN

The stress tensor is given by Murnaghan [15] as

$$\tau_{ij} = \frac{\rho}{\rho_0} \sum_{p,q=1}^{3} \left[\frac{\partial x_i}{\partial a_p}\right]\left[\frac{\partial U}{\partial \eta_{pq}}\right]\left[\frac{\partial x_j}{\partial a_q}\right] \tag{9}$$

where ρ_0 is density of the natural state and ρ is that of the deformed state respectively. x_i are the co-ordinates of the atoms in a homogeneously deformed state and a_i are the position co-ordinates of the atoms in the unstrained state of the hexagonal BN.

Comparing this with the expression

$$\tau_{ij} = -p\delta_{ij} + \sum_{kl} C'_{ijkl}\beta_{kl} \tag{10}$$

where p being the pressure and β_{kl} being the infinitesimal strain parameter, the expressions for the effective second order elastic constants C'_{ijkl} can be obtained to the first order in Lagrangian strains η and ζ [16] as

$$\begin{aligned}
C'_{11} &= C_{11} + \eta(4C_{11} + 2C_{12} + C_{111} + C_{112}) \\
&\quad + \zeta(-C_{11} + 2C_{13} + C_{113}) \\
C'_{12} &= C_{12} + \eta(2C_{12} + C_{111} + 2C_{112} - C_{222}) \\
&\quad + \zeta(-C_{12} + C_{123}) \\
C'_{13} &= C_{13} + \eta(C_{113} + C_{123}) + \zeta(C_{13} + C_{133}) \\
C'_{33} &= C_{33} + \eta(4C_{13} - 2C_{33} + 2C_{133}) \\
&\quad + \zeta(5C_{33} + C_{333}) \\
C'_{44} &= C_{44} + \eta\left(\frac{1}{2}C_{11} + \frac{1}{2}C_{12} + C_{13} + C_{144} + C_{155}\right) \\
&\quad + \zeta\left(\frac{1}{2}C_{13} + \frac{1}{2}C_{33} + C_{44} + C_{344}\right) \\
C'_{66} &= C_{66} + \eta\left(C_{11} + C_{12} + 2C_{66} - \frac{1}{2}C_{112} + \frac{1}{2}C_{222}\right) \\
&\quad + \zeta\left(C_{13} - C_{66} + \frac{1}{2}C_{113} - \frac{1}{2}C_{123}\right)
\end{aligned} \tag{11}$$

To get the pressure derivatives $\frac{dC'_{ij}}{dp}$ we substitute η and ζ to the first order in pressure p as

TABLE IV Pressure derivatives of the second-order elastic constants of hexagonal BN

$\frac{dC'_{ij}}{dp}$	Present work
$\frac{dC'_{11}}{dp}$	9.10
$\frac{dC'_{12}}{dp}$	5.44
$\frac{dC'_{13}}{dp}$	4.43
$\frac{dC'_{33}}{dp}$	15.45
$\frac{dC'_{44}}{dp}$	3.22
$\frac{dC'_{66}}{dp}$	1.84

$$\eta = \frac{(C_{13} - C_{33})p}{(C_{11} + C_{12})C_{33} - 2C_{13}^2}$$

and

$$\zeta = \frac{(2C_{13} - C_{11} - C_{12})p}{(C_{11} + C_{12})C_{33} - 2C_{13}^2} \tag{12}$$

The pressure derivatives are obtained by taking the derivative of Equation 11 with respect to pressure p and substituting the values of second order and third order elastic constants of hexagonal BN given in Tables I and III.

The pressure derivatives of the second order elastic constants for hexagonal boron nitride thus obtained are reported in Table IV.

4. Results and discussion

Hexagonal boron nitride possesses six-second order elastic constants. The values of second order elastic constants of hexagonal boron nitride obtained in the present work are collected in Table II along with experimental value of Green *et al.* [2] and the theoretical value of Kuzuba and Ishi [17]. The elastic constant C_{44} obtained in the present work is in reasonable agreement with the value, calculated by Kuzuba and Ishi. The second order elastic constant C_{11} which corresponds to the elastic stiffness along the basal plane of the crystal is greater than C_{33}. Since C_{33} being the stiffness tensor component along the c-axis of the crystal, this result is expected from a layer-like material like BN, where the binding forces along the ab-plane is much higher than that along the c-axis.

The ten third order elastic constants evaluated in the present work are given in Table 3. The values obtained in the present work are of the same order as that of the experimental value. Magnitude of third-order elastic constants are one order higher than the second order elastic constants expected of a crystalline solid [18]. The pressure derivatives of second-order elastic constants obtained in the present work are presented in Table IV. dC_{33}/dp obtained in the present work is greater than dC_{11}/dp which indicates that the compressibility along c-axis is higher than that along

ab-plane of boron nitride. This corroborates the layer like structure of hexagonal boron nitride.

References

1. B. YATES, M. J. OVERY and O. PIRGON, *Phil. Mag.* **32** (1975) 847.
2. J. F. GREEN, T. K. BOLLAND and J. W. BOLLAND, *J. Chem. Phys.* **64** (1976) 656.
3. C. S. MENON, *Bull. Master. Sci.* **7** (1985) 91.
4. V. L. SOLOZHENKO, T. PEUN, *J. Phys. Chem. Solids* **58** (1997) 1321.
5. V. A. SAVASTENKO and A. U. SHELEG. *Phys. Stat. Sol.* (a) **48** (1978) K135.
6. G. KERN, G. KRESSE and J. HAFNER, *Phys. Rev.* B. **59** (1999) 8551.
7. K. KARCH, F. BECHSTEDT, P. PAVONE and D. STRANCH, *Physica* B **219–220** (1996) 445.
8. V. L. SOLOZHENKO, G. WILL and F. ELF, *Solid State Commun.* **96** (1995) 1.
9. K. KARCH, G. PORTISCH, F. BECHSTEDT, O. PAVONE and D. STRAUCH, in 23rd International Conference on the Physics of Semiconductors (World Scientific, Singapore, 1996) Vol. 1, p. 529.
10. H. W. LEITE-ALVES, J. L. A. ALVES, J. L. P. KASTINEIRA and J. R. LEITE, *Materials Science and Engineering* B, **59** (1999) 264.
11. V. L. SOLOZHENKO, G. WILL, H. HUPEN and F. ELF, *Solid State Commun.* **90** (1994) 65.
12. K. KARDI and F. BECHSTEDT. *Phys. Rev.* B **56** (1997) 7404.
13. KWISENE KIM, R. L. WALTER, LEMBRECHT and B. SEGALL, *ibid.* **53** (1996) 16310.
14. M. BORN and K. HUANG, "Dynamical Theory of Crystal Lattice" (Oxford, London, 1954).
15. F. D. MURNAGHAN, "Finite Deformation of an Elastic Solid" (Wiley, New York, 1951).
16. R. RAMJI RAO and A. PADMAJA, *J. Appl. Phys.* **62** (1987) 440.
17. T. KUZUBA and M. ISHI, *Phys. Stat. Sol* (b) **55** (1989) K13.
18. K. P. JAYACHANDRAN and C. S. MENON, *J. Phys. Chem. Solids* **60** (1999) 267.

Received 19 November 2001
and accepted 6 May 2002